metric structure of the anion (Figure 1). Crystal state symmetry demands that the discrete $(Fe(SR)_4)^-$ anions have the rare S_4 ($\bar{4}$) point group symmetry. The FeS_4 local symmetry is therefore rigorously D_{2d}, compressed from T_d symmetry along the S_4 axis. The two equivalent S–Fe–S angles bisected by the S_4 axis are 114.4 (1)°, while the remaining four angles are equal to 107.08 (5)°. The conformation of the arenethiolate ligands relative to each other and to the FeS_4 core is determined by the angles θ, α, and β. The Fe–S–C angle, θ = 102.4 (2)° is typical;[5,6] both the torsion angles α and β,[10] are nearly 90° and act to create a symmetric conformation, which is not crystallographically required. The conformation of molecule **1** is not distorted in spite of the steric requirements of the ortho-disubstituted ligands.

The geometry of **1** is not only aesthically pleasing but also biologically relevant. Recent refinement of the X-ray crystal structure of oxidized rubredoxin from *Clostridium pasteurianum*[11] shows that the geometry of the $Fe(SCH_2-)_4$ unit as well as the FeS_4 core closely approaches D_{2d} effective symmetry.[12] It is important to consider the position of the α-carbons in this discussion since it is the orientation of these carbons that determines the positioning of the sulfur lone pairs and in turn influences the electronic properties of the FeS_4 centers. When the nonlinearity of the Fe–S–C linkage is taken into account, D_{2d} is the highest possible symmetry for the $Fe(SCH_2-)_4$ unit of rubredoxin. In the protein, the S_4 axis bisects the angles defined as S_6–Fe–S_{39} and S_9–Fe–S_{42}.[13] In contrast to the tetragonal compression along the S_4 axis observed in **1**, the FeS_4 unit in rubredoxin is tetragonally elongated along the S_4 axis.

The electronic and ESR spectral properties of $Fe^{III}(SR)_4$ compounds are quite sensitive to structural distortions of the $Fe(SCH_2-)_4$ unit. The ESR spectrum of **1** shows a sharp resonance at $g = 4.3$ over the temperature range 6–77 K,[14] which is similar to the result reported for rubredoxin.[15] In comparison, the ESR spectrum of **2** at 6 K is more complex, exhibiting resonances at $g = 8.4$ and 5.3 as well as at $g = 4.3$, which reflects the low symmetry of the $Fe(SCH_2-)_4$ unit due to the conformational constraints of the bidentate ligands. Furthermore, the ESR spectrum of desulforedoxin from *Desulfovibrio gigas*[16] is also complex, which may indicate that the protein has a $Fe(SCH_2-)_4$ unit of low symmetry.

Work, using sterically encumbered thiolate ligands to create viable models for the metal center in metalloenzymes, is continuing.

Acknowledgment. We thank Drs. Arthur Forman and Karen Schaich of the Medical Research Center, Brookhaven National Laboratory, for advice and assistance with the ESR spectroscopy and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support.

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Supplementary Material Available: Table of fractional coordinates and thermal parameters (1 page). Ordering information is given on any current masthead page.

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(9) **1** crystallizes as black tetrahedra in the tetragonal space group $I\bar{4}$ with $a = b = 12.366$ (2) Å, $c = 16.352$ (4) Å, $V = 2501$ (1) $Å^3$, and $Z = 2$. The X-ray data were collected on an Enraf-Nonius CAD4A diffractometer using molybdenum radiation. The structure was solved by using Patterson and difference Fourier methods using the computer programs of the Enraf-Nonius structure determination package. The iron atom is located at special position 2a. Final anisotropic refinement of all non-hydrogen atoms using 726 unique reflections with $I > 3\sigma(I)$ gave $R = 0.057$, $R_w = 0.076$.

(10) The torsion angle α(87°) is the dihedral angle made by the Fe–S–C plane with the S–Fe–S′ plane, where S′ is related to S by the C_2 (S_4^2) axis. The torsion angle β (90°) is measured by the angle between the Fe–S–C plane and the plane of the durenethiolate ligand.

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Tetragonal vs. Trigonal Coordination in Copper(II) Complexes with Tripod Ligands: Structures and Properties of $[Cu(C_{21}H_{24}N_4)Cl]PF_6$ and $[Cu(C_{18}H_{18}N_4)Cl]PF_6$

Sir:

There is a great deal of evidence supporting the notion that "Cu(I)-like" environments dominate the coordination chemistry of copper in redox-active metalloproteins. This includes the type I "blue" copper centers in copper electron-transfer proteins and multicopper oxidases[1] as well as the binuclear centers[2] in the oxygen carrier hemocyanin[3] and the monooxygenases tyrosinase and dopamine β-hydroxylase.[2,4] Evidence for coordination numbers of 4 or less,[1,2,5-7] imidazole coordination,[6-8] sulfur ligation,[7] and/or high redox potentials[1,9,10] is consistent with an environment favoring the reduced state of copper in these systems.

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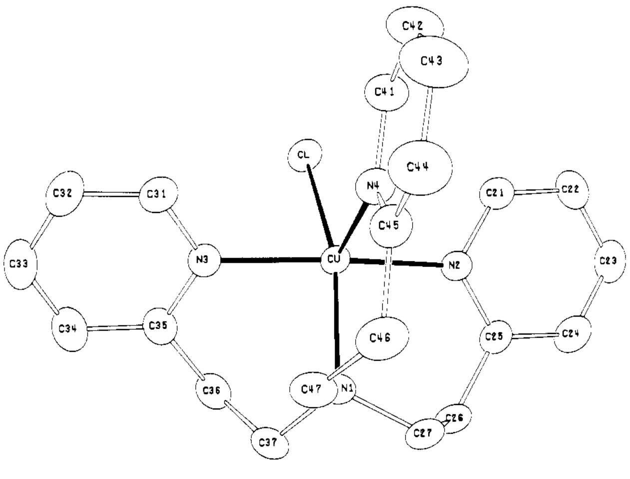
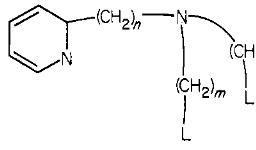


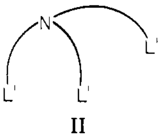
Figure 1. ORTEP drawing of $[Cu(tepa)(Cl)]^+$ (**1**), showing the atom-labeling scheme for the molecule. Relevant bond lengths (Å) and angles (deg): Cu–N(1), 2.100 (3); Cu–N(2), 2.062 (3); Cu–N(3), 2.038 (3); Cu–N(4), 2.227 (3); Cu–Cl, 2.289 (1); N(1)–Cu–N(2), 94.2 (1); N(1)–Cu–N(3), 86.3 (1); N(1)–Cu–N(4), 95.7 (1); N(1)–Cu–Cl, 159.8 (1); N(2)–Cu–N(3), 171.1 (1); N(2)–Cu–N(4), 93.9 (1); N(2)–Cu–Cl, 91.2 (1); N(3)–Cu–N(4), 94.9 (1); N(3)–Cu–Cl, 85.5 (1); N(4)–Cu–Cl, 103.4 (1).

One approach to modeling and studying the redox and coordination chemistry of Cu(I) and Cu(II) of this type is to study complexes of tripodal tetradentate ligands. These have become the subject of extensive investigations by ourselves and others because they may be expected to impart a nonplanar geometry upon copper ions, thus favoring the reduced state. The existence of imidazole from histidine residues as a donor to copper in the proteins has prompted the use of unsaturated nitrogen donors in model studies. Thus, we are carrying out extensive structural and physicochemical studies of Cu(I) and Cu(II) compounds of pyridyl-containing ligands (I).[11,12]



I

L = 2-pyridyl, -SR
$n = 1,2; m = 2,3$



II

L' = 2-pyridyl

Symmetric tripod ligands (II) where L' = 2-benzimidazole,[13-15] thioether,[15,16] pyrazole,[17] and imidazole[18] and their copper complexes have been reported. In all cases, the Cu(II) complexes are five-coordinate $[Cu^{II}(tripod)(X)]^{z+}$ ($z = 1, 2$), but few structural studies have appeared in the literature.[14,17b,19,25] We also have prepared and structurally characterized a variety of compounds of the ligands II, tris(2-(2-pyridyl)ethyl)amine[20] (tepa), and tris(2-pyridyl)methylamine (tmpa). These include the complexes $[Cu^{II}(tripod)X]^{z+}$ ($z = 1, 2$; X = NO_3^-, Cl^-, methylimidazole, N_3^-) as well as the tetracoordinate compound $[Cu(tepa)]BPh_4$.[12] We now wish to report and compare preliminary studies of structural and physical properties of the chloride derivatives $[Cu(tepa)Cl]^+PF_6^-$ (**1**) and $[Cu(tmpa)Cl]^+PF_6^-$ (**2**).[22] These two compounds exhibit markedly different structural behavior. These differences also manifest themselves in their redox and electronic properties, demonstrating the importance of imposed ligand constraints in determining the chemistry of copper moieties.

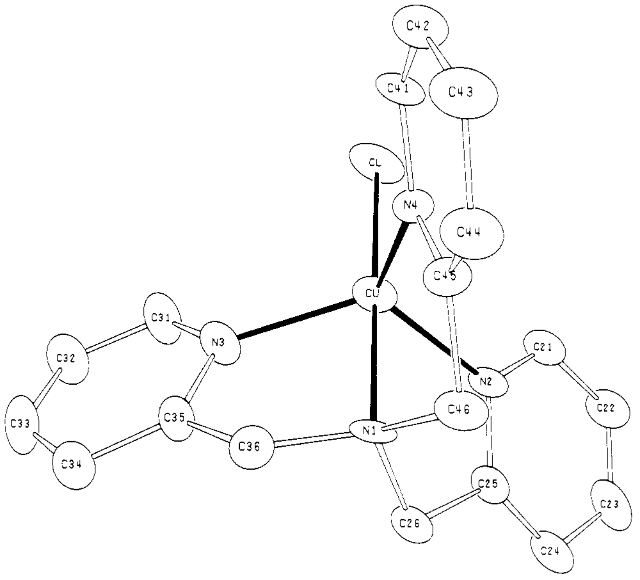


Figure 2. ORTEP drawing of $[Cu(tmpa)(Cl)]^+$ (**2**), showing the atom-labeling scheme for the molecule. Relevant bond lengths (Å) and angles (deg): Cu–N(1), 2.050 (6); Cu–N(2), 2.062 (8); Cu–N(3), 2.060 (9); Cu–N(4), 2.072 (6); Cu–Cl, 2.233 (2); N(1)–Cu–N(2), 81.5 (4); N(1)–Cu–N(3), 81.1 (4); N(1)–Cu–N(4), 80.8 (3); N(1)–Cu–Cl, 179.1 (4); N(2)–Cu–N(3), 118.2 (3); N(2)–Cu–N(4), 118.8 (3); N(2)–Cu–Cl, 97.6 (3); N(3)–Cu–N(4), 116.0 (3); N(3)–Cu–Cl, 99.6 (3); N(4)–Cu–Cl, 99.4 (2).

As reported,[12] $Cu^I(tepa)BPh_4$ displays a pseudotetrahedral coordination that is distorted toward a pyramidal geometry. This arrangement allows facile approach and coordination of a fifth ligand, chloride, in the corresponding Cu(II) complex (Figure 1).[23] Distortions occur however, and one of the Cu^{II}–N_{py} bond distances (Cu–N(4)) increases significantly (ca. 0.20 Å) to 2.227 (3) Å, while the others change only slightly.[24] The accompanying bond angle deformations result in a roughly square-pyramidal coordination geometry with pyridine N(4)

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[20] tepa was synthesized by reaction of excess 2-vinylpyridine with ammonium acetate in methanol. Removal of solvent, extraction into CH_2Cl_2 from 20% NaOH(aq), and drying over $MgSO_4$ were followed by column chromatography (silica gel–MeOH).

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[22] Complexes were synthesized by addition of $CuCl_2$ to the tripod ligand in methanol, followed by precipitation using excess methanolic $NaPF_6$. Recrystallization of analytically pure complexes **1** and **2** was effected in CH_2Cl_2–C_6H_{12}.

[23] $[Cu(tepa)Cl](PF_6)$ crystallizes in the monoclinic space group $P2_1/c$ with $a = 12.483$ (2) Å, $b = 12.939$ (2) Å, $c = 16.268$ (2) Å, $\beta = 90.20$ (1)°, $V = 2627.6$ (8) Å^3, and $Z = 4$. The structure analysis is based on 3516 independent reflections that have been refined to a R value of 0.044 (Mo Kα $\lambda = 0.71069$ Å).

[24] The Cu–N_{py} bond lengths in $Cu(tepa)BPh_4$ are 2.021 (5), 2.012 (5), and 2.022(5) Å.[12]

in the axial position. Structural studies completed on the related complexes $[Cu^{II}(tepa)X]^{z+}$ (X = NO_3^-,[11e] Me-Im[12]) show the same effect, where one Cu^{II}–N_{py} distance is ca. 0.18 Å longer than the others.

In contrast, the structure of $[Cu^{II}(tmpa)Cl]^+$ is very close to trigonal bipyramidal as indicated by the near equivalence of the Cu–N bond lengths and all related bond angles (Figure 2).[25] The analysis of important dihedral angles supports this description and contrasts greatly with that for the tepa complex.[26]

Physicochemical properties of **1** and **2** in solution are also consistent with the structural results and the differences described. $[Cu(tepa)Cl]PF_6$ shows a visible absorption band maximum at 665 nm (ϵ 200) with a low-energy shoulder (λ 967 nm, ϵ 48), while the spectrum of $[Cu(tmpa)Cl]PF_6$ has a reversed appearance with a band at 962 (ϵ 210) and a high-energy shoulder at 632 nm (ϵ 88) (CH_3CN solutions). These data are consistent with a square-pyramidal coordination for **1** and trigonal bipyramidal for **2**.[27] The electron spin resonance spectrum of frozen solutions of all pentacoordinate Cu(II) complexes of tepa exhibit typical axial spectra with well-resolved Cu hyperfine splittings in the parallel region.[28] On the other hand, **2** shows a reversal of parallel and perpendicular regions ($g_\parallel < g_\perp$) as expected for trigonal-bipyramidal Cu(II) compounds[29] and consistent with that observed in a number of Cu(II) complexes with tripod ligands.[13-15,27,30] Again, $[Cu^{II}(tmpa)X]^{z+}$ (z = 1, 2; X = Me-Im, N_3^-) exhibit analogous behavior.

There are also considerable differences in the redox behavior of **1** and **2**. Cyclic voltammetric experiments[31] indicate both chloride complexes are well-behaved and give quasi-reversible redox waves with $E_{1/2} = +0.17$ V for **1** and $E_{1/2} = -0.39$ V for **2**. The difference of 0.56 V in the reduction potential of these complexes could be explained in part by the expected relative instability of a Cu(I) analogoue of tmpa in which only five-membered chelate rings would be formed.[33] In a series of copper complexes containing tripod ligands, we have found that each change of a chelate ring from six to five membered results in a lowering of the Cu(II)–Cu(I) redox potential by ~0.2 V.[34]

In conclusion, Cu(II) complexes containing tripodal tetradentate ligands can have trigonal or tetragonal coordination environments depending on whether one or two methylene groups separate adjacent donor functions. These variations dictate differences in the electronic properties as manifested by the ESR and absorption spectra of these compounds. The complexes described thus provide a structural basis for variations observed in other studies of tripodal Cu(II) complexes.[13-15]

Continuing studies on these and related compounds will help to elucidate reactivity and structure–function relationships for the copper ion sites of redox-active proteins.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work (K.D.K.). We also thank the Research Corp. (K.D.K.) and the National Institutes of Health (K.D.K. and J.Z.). Helpful discussions concerning EPR studies with Professor G. F. Kokoszka are also acknowledged.

Registry No. **1**, 82871-02-1; **2**, 82865-79-0.

Supplementary Material Available: Listings of positional and isotropic thermal parameters, anisotropic thermal parameters, bond lengths, and bond angles (11 pages). Ordering information is given on any current masthead page.

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(25) $[Cu(tmpa)Cl]PF_6$: orthorhombic space group *I2ab*; a = 14.924 (3), b = 16.632 (4), c = 17.346 (3) Å; V = 4305.6 (16) Å^3; Z = 8. An R value of 0.063 was obtained from refinement of 1793 independent reflections (Mo Kα, $\bar{\lambda}$ = 0.71069 Å).

(26) The shape determining angles e_1, e_2, and e_3 for **2** are 51.3, 53.0, and 52.6° compared to the values of $e_1 = e_2 = e_3 = 53.1°$ for an idealized trigonal-bipyramidal geometry. For **1**, e_1, e_2, and e_3 are 75.1, 71.8, and 11.6° compared to 75.7, 75.7, and 0.0° for an idealized square-based pyramid. See: Muetterties, E. L.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1974**, *96*, 1748.

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(28) For **1**: $g_\parallel = 2.23$, $A_\parallel = 162 \times 10^{-4}$ cm^{-1} (DMF–$CHCl_3$).

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(31) Dimethylformamide solvent; 0.11 M tetra-*n*-butylammonium hexafluorophosphate supporting electrolyte; glassy-carbon working electrode. Potentials are vs. NHE where ferrocene is used as calibrant.[32] Complex **2** is well-behaved with the peak current ratio $i_a/i_c = 0.95$ and cathodic to anodic peak separations approaching those of ferrocene. For **1**, a kinetic barrier to electron transfer is indicated by considerably larger peak separations that decrease with decreasing scan rate (180 mV at 50 mV/s) ($i_a/i_c \approx 0.8$).[34b]

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High-Pressure Temperature-Jump Evidence for an I_a Mechanism for Substitution Reactions of Manganese(II) in Aqueous Solution

Sir:

In a series of papers[1] Merbach and co-workers reported high-pressure NMR evidence for a gradual mechanistic changeover from I_a to I_d for solvent-exchange reactions on divalent octahedral first-row transition-metal ions. They reported[1-3] negative volumes of activation for the exchange of CH_3OH and H_2O on Mn(II) and positive values for the exchange of CH_3OH and H_2O on Fe(II) and for the exchange of CH_3OH, H_2O, CH_3CN, and DMF on Co(II) and Ni(II). These results were interpreted as evidence for I_a and I_d exchange mechanisms,[4] respectively, resulting in the mentioned gradual mechanistic changeover along the first-row transition-metal ions. The above series was recently extended to include the hexaaquated V(II) ion, for which a volume of activation of -4.1 ± 0.1 cm^3 mol^{-1} for the water-exchange process was reported.[5] This result further confirms the earlier observed tendency.[1]

Complex formation reactions of such solvated metal species are generally controlled by, or strongly related to, the solvent-exchange process. Only few pressure dependence studies of fast (T-jump) substitution reactions of divalent first-row

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